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VIBRATIONAL DEACTIVATION OF HF($v=1$) AND
DF($v=1$) BY H AND D ATOMS

R. F. Heidner, III, et al

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$v = 1$ level. A verification of the method was made by determining a rate coefficient for $H + HCl(v = 1)$ that is in good agreement with a recent study.

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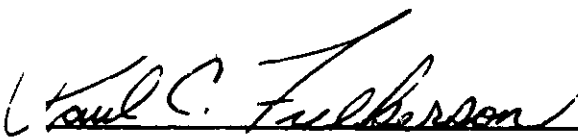
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 Paul C. Fulkerson, 2nd Lt, USAF
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PREFACE

The authors gratefully acknowledge many conversations with Drs. R. L. Wilkins, M. A. Kwok, and N. Cohen and discussions with Mr. G. P. Quigley and Professors H. F. Schaefer, III, and D. G. Truhlar. Expert technical and computer programming assistance was provided by Carrol Gardner and Karen Foster, respectively.

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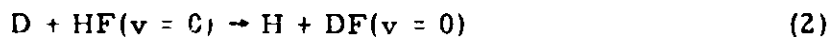
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1. INTRODUCTION

Successful operation of chemical lasers requires that the pumping of excited vibrational levels be rapid with respect to collisional removal and decay by spontaneous emission. In the $F + H_2$ chemical laser, the reaction



provides a population inversion. Vibrationally excited HF can be deactivated by H_2 , F, H, buffer gas, and by HF itself. Rate coefficients for $HF(v = 1)$ quenching by HF,¹ H_2 ,²⁻⁵ and F ⁶ have been determined experimentally. Classical trajectory calculations^{7,8} for $H + HF(v \geq 1)$ indicate that H atoms can be the dominant deactivator in hydrogen halide laser systems. Measurements for $H + HF(v = 2, 3)$ deactivation made by Kwok and Wilkins⁹ are in good agreement with the trajectory calculations. For $H + HF(v = 1)$, Kwok and Wilkins found a rate coefficient slightly smaller than predicted, while Quigley and Wolga⁶ recently reported an upper limit that is more than two orders of magnitude smaller. In this paper, we present kinetic measurements for the deactivation of $HF(v = 1)$ and $DF(v = 1)$ by H and D atoms at $T = 295$ K. These data were obtained by means of the techniques of laser-induced fluorescence²⁻⁵ for HF vibrational relaxation measurements and isothermal calorimetry¹⁰ for the H-atom concentration measurements. An upper limit for the rate of the reaction



was estimated. The present results are useful in evaluating the potential energy surfaces used for $H + HF$ in the published trajectory calculations. A measurement of the process $H + HCl(v = 1)$, confirming a recent study by Arnoldi and Wolfrum,¹¹ is presented for comparison with the data for HF and DF .

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. FLOW SYSTEM

The experimental apparatus used in this study is shown in Fig. 1. The fluorescence cell was constructed of 22-mm i.d. pyrex tubing with window flanges cut on three sides such that the distance from tube center to each window was 14 mm. The inside of the cell, including the sapphire windows, was coated to reduce atom recombination and loss of HF at the walls. When first applied, teflon coatings¹² were quite effective; however, it was found that the coatings were slowly degraded by HF. Halocarbon wax (Halocarbon, Inc.) coatings were used reproducibly to maintain high H-atom concentrations ($\sim 5 \times 10^{15}$ cc) in the presence of HF. The kinetic results were the same with either coating. Hydrogen and deuterium atoms were produced by a 2450-MHz microwave discharge in He-H₂ or He-D₂ mixtures. The microwave power coupled to the 10-mm i.d. quartz discharge tube was ≤ 50 W. Downstream of the discharge, the walls were coated as previously described. Approximately 7 cm upstream of the fluorescence region, HF was mixed into the gas stream. All experiments were run at partial pressures of 1 to 3.5, 0.01 to 0.05, and 0.1 to 1 Torr for He, HF, and H₂, respectively. At low H₂ partial pressures, approximately 40% of the H₂ was dissociated. Mass flows were measured with rotating ball flowmeters calibrated by pressure-rise measurements in a standard volume. Flow velocity in the fluorescence region was typically 300 cm/sec.

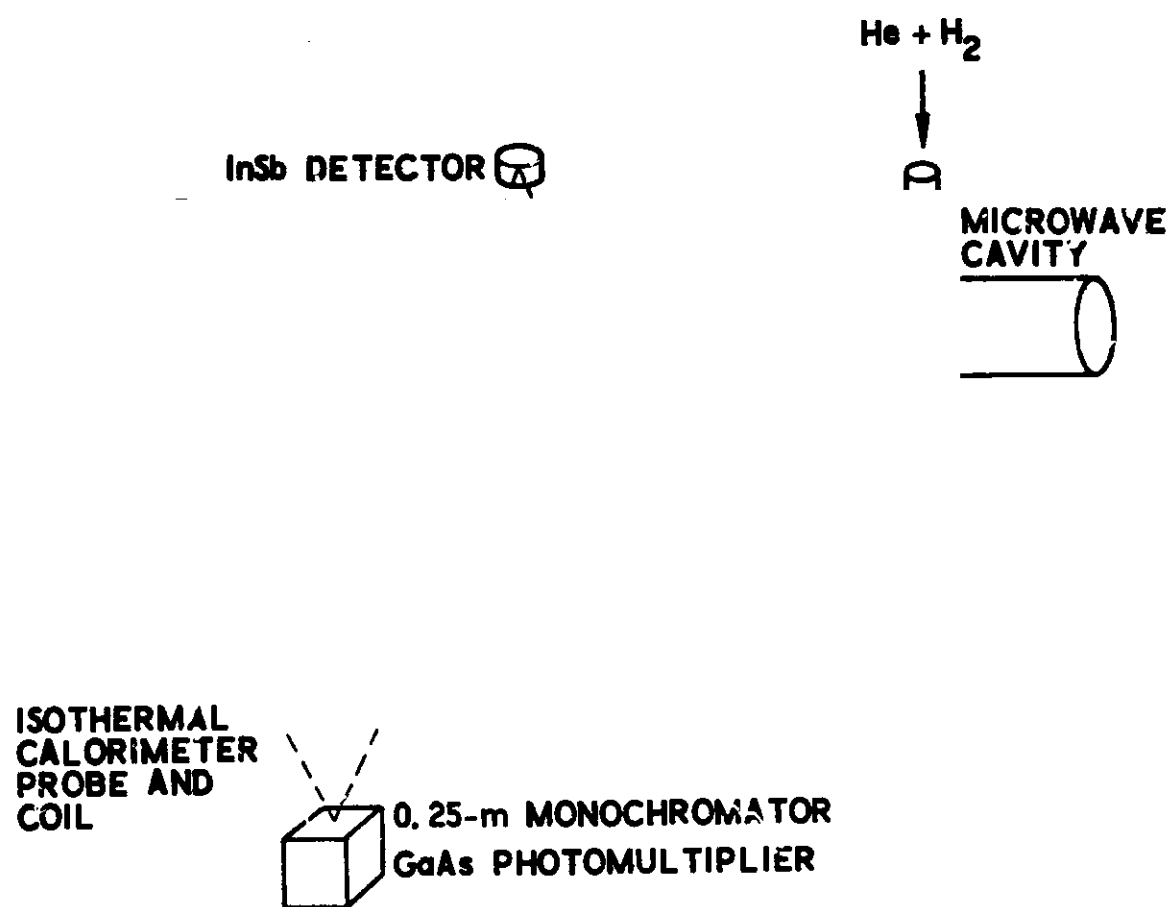


Fig. 1. Apparatus

B. LASER-INDUCED FLUORESCENCE

The use of a pulsed laser to pump a small amount of HF(DF, HCl) to the $v = 1$ level has been described previously.^{1, 4} Briefly, the TEA laser operates by repetitively discharging a 3000-pF capacitor at 20 kV through an SF₆-H₂(D₂) mixture. For the HCl($1 \rightarrow 0$) laser, a mixture of H₂ + Cl₂ was used. The laser pulse passes through the fluorescence cell twice, and the induced fluorescence is observed perpendicular to the direction of excitation. The fluorescence region is focused onto a liquid-nitrogen-cooled InSb detector with an $f/1.5$ CaF₂ lens system. An ac-coupled amplifier (Perry Model 050, gain = 100) is housed in proximity to the detector in a doubly shielded box. The output signal is displayed on an oscilloscope, and the decay traces are recorded on Polaroid film.

C. ISOTHERMAL CALORIMETER

The isothermal calorimeter consists of a movable coil of 0.01-in. - diam 90% Pt 10% Rh wire wound into an hour-glass shape with a 0.75-in. maximum diameter. The coil is supported on W rods covered with teflon sleeving. Catalytic efficiency is regenerated periodically by electro-deposition of Pt black on the coil. The probe can be translated axially along the cell to a point very close to the fluorescence region in order to measure the rate of wall removal of the H atoms. The probe usually was positioned in the system approximately 5 cm downstream of the fluorescence region and suffered no ill effects from the small quantity of HF in the system. Measurements of H-atom concentrations were unaffected by the presence of HF.

The isothermal catalytic probe serves as one arm of the self-balancing Kelvin bridge described by Trainor et al.¹³ The control circuit supplies sufficient current (~1 amp) to heat the probe to an elevated temperature such that its resistance equals the resistance of the standard bridge resistor (~3 Ω). The electrical power supplied to the probe can be calculated from this standard resistance and the current through the probe coil. Recombination of H atoms on the probe reduces the amount of external power required to maintain the probe at elevated temperature (~150 C) and resistance. This decrease in external power is a direct measure of the mass flow rate of H atoms.^{10, 13, 14}

Before isothermal calorimetry can be used to measure absolute atom densities, the following must be determined: (1) the accommodation of the recombination energy on the surface of the platinum coil, (2) the efficiency of the coil for recombining the atoms, and (3) the sensitivity of the coil to electronically or vibrationally excited species. Trainor et al.¹³ recently measured the accommodation coefficient for the heat released by the recombination of H atoms on Pt. They found it to be near unity by comparing the probe measurements with a second absolute measure of H atoms, i.e., chemical titration with NOCl. This observation is supported by work by Heidner.¹⁵ No $H_2(v = 1)$ was observed by means of the vacuum ultraviolet absorption spectrum when H atoms recombined on a Pt coil.

Several experiments were conducted to measure probe efficiency and linearity. Relative H-atom concentrations upstream and downstream of the probe were measured by the NO gas-titration method of Clyne and Thrush.¹⁶

The $(0,0,0) \rightarrow (0,0,0)$ band of HNO^* at 760 nm was monitored with a Bausch and Lomb high-intensity monochromator and a GaAs photomultiplier. The HNO^* fluorescence signal in this experiment showed that greater than 95% of the H atoms were removed on the probe. The intensity of the HNO^* fluorescence is linear with NO mass flow rate for constant $[\text{H}]$ (Fig. 2) and linear with the power dissipated by the recombining atoms on the coil for constant $[\text{NO}]$ (Fig. 3). The nonzero intensity at $\Delta W = 0$ (Fig. 3) probably is due to the underlying NO_2^* continuum.¹⁶

No signal was measured on the probe (< 3 mW) when pure He was passed through the discharge. This demonstrates that there is no gas heating caused by the discharge that persists into the fluorescence region. Metastable electronic levels of H atoms or H_2 cannot survive the transit time from the discharge to the fluorescence cell nor can vibrationally excited H_2 that is rapidly deactivated in the presence of H atoms.¹⁴

D. MATERIALS

Hydrogen fluoride (Matheson Co., 99.9%, in liquid phase) and deuterium fluoride (Ozark Mahoning, 98%, in liquid phase) were purified by pumping on samples at 77 K to remove $\text{H}_2(\text{D}_2)$ and then distilling into a passivated 4-liter stainless-steel tank. These gases were usually diluted 1:1 in Ar to a total sample pressure of 1 atm. Hydrogen chloride (Matheson, 99%) was used without purification and dilution; Cl_2 (Matheson, 99.9%) was used in the HCl laser without purification. Helium (Air Products, 99.995%) was passed through a molecular sieve trap that was periodically baked-out under vacuum at elevated temperature. Hydrogen (Matheson, 99.95%) and deuterium (Oak Ridge, $> 98\%$) were

NO MOLAR FLCW, $\mu\text{mol/sec}$

Fig. 2. Comparison of isothermal calorimeter and nitric oxide titration for linear relation of HNO^* fluorescence with the addition of NO at constant $[\text{H}]$

PROBE POWER FROM ATOM RECOMBINATION
 ΔW , MW

0 10 20 30 40
 I_{HNO^*} , arbitrary units

Fig. 3. Comparison of isothermal calorimeter and nitric oxide titration for linear relation of H-atom recombination power with HNO^* fluorescence at constant $[\text{NO}]$

intentionally not purified, since purification caused a marked reduction in the production of atoms. In fact, minute amounts of H_2O were generally added in a controlled manner to the H_2 and D_2 flows to catalyze large atom production.¹⁷ Water was added by passing $H_2(D_2)$ through a cold trap containing H_2O (s) at either -23 or -196 C. Nitric oxide (Air Products, 99.0%) was purified by passing the gas through a trap containing Ascarite cooled to -78 C and then redistilling a sample from -150 to -193 C. Sulfur hexafluoride (Matheson, 99.8%) was used in the pulsed laser without further purification.

III. RESULTS

A. VIBRATIONAL-RELAXATION MEASUREMENTS

Fluorescence decay times measured with and without the microwave discharge are listed in Tables 1 through 4 for the four combinations of HF($v = 1$) and DF($v = 1$) deactivation by H and D atoms. The total pressure and the concentration of H and D atoms are also listed. In the analysis of the data, it was assumed that spontaneous emission, diffusion and convection losses, quenching by He, and self-quenching by HF do not change when atoms are produced by the microwave discharge. If these loss terms are combined as the decay time τ and the decay times in the absence and presence of the discharge are given by τ_1 and τ_2 , respectively, then

$$\frac{1}{\tau_1} = k_{\text{HF-H}_2} [\text{H}_2]^0 + \frac{1}{\tau} \quad (3)$$

$$\frac{1}{\tau_2} = k_{\text{HF-H}_2} \left([\text{H}_2]^0 - \frac{1}{2} [\text{H}] \right) + k_{\text{HF-H}} [\text{H}] + \frac{1}{\tau} \quad (4)$$

$$\frac{1}{\tau_2} - \frac{1}{\tau_1} = \left(k_{\text{HF-H}} - \frac{1}{2} k_{\text{HF-H}_2} \right) [\text{H}] \quad (5)$$

where $[\text{H}_2]^0$ is the concentration of H_2 without the discharge and $k_{\text{HF-H}_2}$ and $k_{\text{HF-H}}$ are the rate constants for HF($v = 1$) deactivation by H_2 and H, respectively. The concentration of H_2 can be significantly reduced by the production of H atoms [Eq. (4)], and τ_2 can be longer than τ_1 if H atoms have

Table 1. Vibrational Relaxation of HF($v = 1$) by H Atoms

Run	P, Torr	[H] $\times 10^9$, mol/cc	τ_{on} , μsec	τ_{off} , μsec	$\Delta(1/\tau)$, sec^{-1}	$\Delta(1/\tau)_{\text{corr}}$, sec^{-1}	$1/k_{\text{HF-H}} - 1/2 k_{\text{HF-H}_2}$ $\times 10^{-11}$, cc/mol-sec	$k_{\text{HF-H}} \times 10^{11}$, cc/mol-sec
1	1.14	3.5	163 ± 7	158 ± 7	-190 ± 380	-90 ± 400	-0.3 ± 1.2	1.3 ± 1.2
2	1.10	2.7	194 ± 10	184 ± 10	-280 ± 400	-180 ± 420	-0.66 ± 1.5	0.9 ± 1.5
3	1.25	1.9	90 ± 5	95 ± 5	580 ± 810	680 ± 850	3.7 ± 4.5^a	5.2 ± 4.5^a
4	1.10	6.1	125 ± 4	121 ± 4	-260 ± 370	-60 ± 400	-0.11 ± 0.68	1.5 ± 0.68
5	2.6	8.6	168 ± 7	168 ± 7	0 ± 350	120 ± 370	0.14 ± 0.43	1.7 ± 0.43
6	1.7	7.0	147 ± 6	143 ± 6	-190 ± 400	-70 ± 430	-0.1 ± 0.61	1.49 ± 0.61
Average value:							-0.21 ± 0.4^b	1.4 ± 0.4^b

^aDatum rejected for being outside 95% confidence limits.

^bMean value of the data. Quoted error is an estimate of the deviation from the mean plus a 10% systematic error in $k_{\text{HF-H}} - 1/2 k_{\text{HF-H}_2}$.

NOTES

1. The H_2 passed through cold trap at 77 K in Runs 1-3 and at 250 K in Runs 4-6.
2. $k_{\text{HF-H}_2} = 3.16 \times 10^{11}$ cc/mol-sec was taken from Ref. 3; also, see Refs. 2 and 4.
3. See text for explanation of H_2O correction in $\Delta(1/\tau)_{\text{corr}}$.

Table 2. Vibrational Relaxation of HF($v = 1$) by D Atoms

Run	P, Torr	[H] $\times 10^9$, mol/cc	τ_{on} , μsec	τ_{off} , μsec	$\Delta(1/\tau)$, sec^{-1}	$\Delta(1/\tau)_{corr}$, sec^{-1}	$k_{HF-D} - 1/2 k_{HF-D_2}$ $\times 10^{-10}$, cc/mol-sec	$k_{HF-D} \times 10^{-10}$, cc/mol-sec
1	1.2	6.4	294 ± 15	280 ± 14	-170 ± 250	-70 ± 270	-1.1 ± 4.2	1.8 ± 4.2
2	1.1	6.5	334 ± 15	304 ± 15	-300 ± 210	-200 ± 230	-3.0 ± 3.6	-0.1 ± 3.6
3	1.03	5.8	374 ± 20	364 ± 20	-70 ± 210	27 ± 230	0.45 ± 3.9	3.4 ± 3.9
4	0.29	2.8	192 ± 10	204 ± 10	310 ± 360	310 ± 360	11 ± 13^a	14 ± 13^a
5	2.28	7.1	420 ± 20	420 ± 20	0 ± 160	-50 ± 170	-0.7 ± 2.4	2.2 ± 2.4
6	1.53	7.7	384 ± 19	338 ± 16	-350 ± 200	-230 ± 220	-3.0 ± 3.0	-0.1 ± 3.0
7	1.28	5.8	170 ± 8	166 ± 8	-140 ± 400	-40 ± 420	-0.7 ± 7.2	2.2 ± 7.3
8	2.12	5.6	508 ± 25	504 ± 25	-20 ± 140	10 ± 150	0.2 ± 2.6	3.1 ± 2.6
Average value:							-1.12 ± 1.5^b	1.8 ± 1.5^b

^a Datum rejected for being outside 95% confidence levels.

^b Mean value of the data. Quoted error includes one standard deviation from the mean plus a 10% systematic error in $k_{HF-D} - 1/2 k_{HF-D_2}$.

NOTES

1. D₂ passed through cold trap at 77 K.
2. $k_{HF-D_2} = 5.8 \times 10^{10}$ cc/mol-sec was taken from Ref. 3; also, see Ref. 2.
3. See text for explanation of H₂O correction in $\Delta(1/\tau)_{corr}$.

Table 3. Vibrational Relaxation of DF($v = 1$) by H Atoms

Run	P, Torr	[H] $\times 10^9$, mol/cc	τ_{on} , μsec	τ_{off} , μsec	$\Delta(1/\tau)$, sec^{-1}	$\Delta(1/\tau)_{\text{corr}}$, sec^{-1}	$k_{\text{DF-H}} - 1/2 k_{\text{DF-H}_2}$ $\times 10^{-10}$, cc/mol-sec	$k_{\text{DF-H}} \times 10^{-10}$, cc/mol-sec
1	2.25	4.2	755 ± 40	800 ± 40	75 ± 90	174 ± 110	4.1 ± 2.7	4.7 ± 2.7
2	2.9	4.0	775 ± 40	885 ± 40	160 ± 80	260 ± 104	6.5 ± 2.6	7.1 ± 2.6
3	2.6	3.7	835 ± 40	870 ± 40	48 ± 78	148 ± 98	4.0 ± 2.7	4.6 ± 2.7
4	1.18	7.2	282 ± 15	288 ± 12	70 ± 240	330 ± 290	4.6 ± 4.0	5.2 ± 4.0
5	1.28	5.9	298 ± 15	296 ± 15	-23 ± 240	380 ± 320	6.4 ± 5.4	7.0 ± 5.4
6	1.40	6.2	288 ± 15	290 ± 15	20 ± 250	690 ± 390	11.1 ± 6.1	11.7 ± 6.2
7	1.58	5.8	202 ± 10	200 ± 10	-50 ± 350	1320 ± 620	22.8 ± 18.8^a	23.4 ± 10.8^a
Average value:							6.1 ± 1.5^b	6.7 ± 1.5^b

^a Datum is rejected for being outside 95% confidence levels.

^b Mean value of the data. Quoted error includes one standard deviation from the mean plus a 10% systematic error in $k_{\text{DF-H}} - 1/2 k_{\text{DF-H}_2}$.

NOTES

1. H_2 passed through cold trap at 77 K in Runs 1-3 and at 250 K in Runs 4-7.
2. $k_{\text{DF-H}_2} = 1.22 \times 10^{10}$ was taken from Ref. 18.
3. See text for explanation of H_2O correction in $\Delta(1/\tau)_{\text{corr}}$.

Table 4. Vibrational Relaxation of DF($v = 1$) by D Atoms

Run	P, τ_{off}	[D] $\times 10^9$, mol/cc	τ_{on} , μsec	τ_{off} , μsec	$\Delta(1/\tau)$, sec^{-1}	$(1/\tau)_{\text{corr}}$, sec^{-1}	$k_{\text{DF-D}} \cdot 1/2 k_{\text{DF-D}_2}$ $\times 10^{-11}$, cc/mol-sec	$k_{\text{DF-D}} \times 10^{-11}$, cc/mol-sec
1	1.02	5.3	220 ± 17	170 ± 10	-1340 ± 500	-1240 ± 510	-2.3 ± 1.0	-0.6 ± 1.0
2	2.23	6.4	170 ± 8	138 ± 6	-1360 ± 870	-1260 ± 890	-2.0 ± 1.4	-0.2 ± 1.4
3	2.15	3.6	372 ± 18	290 ± 15	-150 ± 240	-660 ± 260	-1.9 ± 0.7	-0.1 ± 0.7
4	3.00	4.4	346 ± 18	270 ± 14	-810 ± 270	-710 ± 290	-1.6 ± 0.7	0.1 ± 0.7
5	1.27	7.1	87 ± 4	65 ± 3	-3900 ± 1900	-3100 ± 2000	-4.4 ± 2.8	-2.7 ± 2.6
6	1.20	6.7	94 ± 4	94 ± 4	0 \pm 960	590 ± 1080	0.9 \pm 1.6	2.6 \pm 1.6
7	1.10	4.7	154 ± 7	131 ± 5	-1100 ± 720	-790 ± 790	-1.7 ± 1.7	3.1 ± 1.7
Average value:							-1.26 ± 0.8^a	-0.1 ± 0.8^a

^a Mean value of the data. Quoted error includes one standard deviation from the mean, 0.58×10^{11} , plus 10% of the mean of $(k_{\text{DF-D}} - 1/2 k_{\text{DF-D}_2})$ for possible systematic error.

NOTES

1. D₂ passed through cold trap at 77 K in Runs 1-4 and at 250 K in Runs 5-7.
2. $k_{\text{DF-D}_2} = 3.5 \times 10^{11}$ cc/mol-sec was taken from Refs. 5 and 19.
3. See text for explanation of H₂O correction in $\Delta(1/\tau)_{\text{corr}}$.

less than half the quenching efficiency of H_2 . An inspection of Eq. (5) reveals that one measures $k_{HF-H} = 1/2 k_{HF-H_2}$. For all four isotopic experiments, the measured difference in decay rates, i.e., $1/\tau_2 - 1/\tau_1$, was very small. In addition, this measured difference must be corrected for the small amount of H_2O required for the efficient production of H atoms. Water is a fast deactivator² of $HF(v = 1)$, and it is partially dissociated to less efficient quenchers by the discharge. Values of $\Delta(1/\tau_{H_2O})$ were estimated experimentally for each run by measuring the fluorescence decay times with H_2 replaced by an identical flow of He through the H_2 flow line. Thus, the values of $1/\tau_2 - 1/\tau_1$ listed in Tables 1 through 4 are corrected by means of Eq. (6).

$$\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)_{\text{corr}} = \left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)_{\text{obs}} - \Delta\left(\frac{1}{\tau_{H_2O}}\right) \quad (6)$$

We have estimated the uncertainties in the measured quantities τ_1 , τ_2 , H , and $\Delta(1/\tau_{H_2O})$. The resulting uncertainties in the values of $k_{HF-H} = 1/2 k_{HF-H_2}$ calculated from Eq. (5) are generally consistent with the sample standard deviation σ_x calculated for each data set. For the $H + HF$ data, the standard deviation from the mean σ_x is much smaller than the estimate of the experimental uncertainties. We report the larger value since the number of data points is small for reliable statistical analysis. The reported values for $k_{HF-D} = 1/2 k_{HF-D_2}$, $k_{DF-H} = 1/2 k_{DF-H_2}$, and $k_{DF-D} = 1/2 k_{DF-D_2}$ are the mean of the measurements in Tables 2 through 4, respectively, with an uncertainty equal to the sum of σ_x and a systematic error (from flow rates,

decay times, and atom concentration) of $\pm 10\%$. For $k_{\text{HF-H}} = 1/2 k_{\text{HF-H}_2}$, the error reported is an estimate of the deviation from the mean plus a 10% systematic error. None of the values reported includes either the random or systematic error in the molecular rate coefficient, i.e., $k_{\text{HF-H}_2}$. Of the four rate coefficients reported, the absolute value of $k_{\text{DF-D}}$ is by far the most sensitive to an error in $k_{\text{DF-D}_2}$.

There are two ways by which the precision of the quantity $k_{\text{HF-H}} = 1/2 k_{\text{HF-H}_2}$ can be improved in these experiments. One method is to increase the concentration of H atoms; however, this as yet has not been accomplished. Another method is to improve the precision of $1/\tau_2 - 1/\tau_1$. An uncertainty of $\pm 5\%$ is assigned to the measured τ values. The apparent precision can be greatly improved by signal-averaging; however, subtle systematic errors such as gas heating of a few degrees might then become important. It would be ideal to find an H-atom precursor that does not deactivate $\text{HF}(v = 1)$. Unfortunately, most such precursors deactivate $\text{HF}(v = 1)$ more rapidly than does H_2 , and they also introduce free radicals with unknown quenching efficiencies for HF.

Experimental data obtained for the relaxation of $\text{HCl}(v = 1)$ by H atoms are plotted in Fig. 4. For these data, τ_2 was much shorter than τ_1 [Eq. (5)]; hence, the deduced rate coefficient $k_{\text{HCl-H}}$ is much larger and much more precise than those for $\text{HF}(\text{DF})$. A small correction to the H-atom concentration (13%) must be made to account for loss between the fluorescence region and the probe. This H-atom loss results from the following reactions²⁰

0

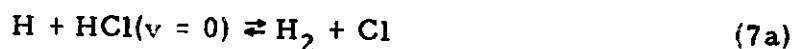
1

2

3 x 10

[H], mol/cc

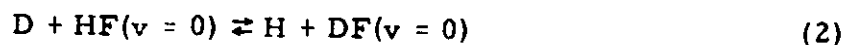
$$k_{\text{HCl-H}} = (4.1 \pm 0.4) \times 10^{12} \text{ mol/sec.}$$



The value of $(4.1 \pm 0.4) \times 10^{12}$ cc/mol-sec obtained here is in excellent agreement with the data of Arnoldi and Wolfrum,¹¹ who obtained $k_{\text{HCl-H}} = (3.9 \pm 1.3) \times 10^{12}$ cc/mol-sec. They used a chemical titration technique to measure [H].

B. FLUORINE-ATOM EXCHANGE

Two experiments were performed to estimate the rate coefficient for the forward reaction



This measured rate coefficient provides a direct test of the surface used in the classical trajectory calculations.^{8, 21} These calculations were made on the basis of a 1.5 kcal/mol barrier for exchange Reaction (2) and yielded the large room-temperature rate coefficient of 7.5×10^{11} cc/mol-sec (Table 5). In the first experiment, the laser-induced fluorescence from $\text{HF}(v = 1)$ was recorded in a flowing mixture of HF, D_2 , and He with and without the microwave discharge. The HF was added to the mixture 20 msec upstream of the fluorescence region. The fluorescence intensity extrapolated to zero time following the laser pulse is proportional to $[\text{HF}(v = 0)]$ for weak absorption of the laser radiation and low self-absorption of the induced fluorescence.

Table 5. Rates of Vibrational Deactivation of HF($v = 1$), DF($v = 1$) by H and D Atoms ($T = 300^\circ\text{K}$)

Process	Wilkins ^{8, 21} (Classical Trajectory)		(¹)	Quigley and Wolga ⁶ (Experimental)	This Work
	k_R^a cc/mol-sec	k_N^b cc/mol-sec	$k_R + k_N$ cc/mol-sec	$k_R + k_N$ cc/mol-sec	$k_R + k_N$ cc/mol-sec
H + HF($v = 1$)	1.7×10^{12}	5.3×10^{11}	$< (7 \pm 4) \times 10^{11}$	$\leq 9 \times 10^9$	$(1.4 \pm 0.4) \times 10^{11}$
H + DF($v = 1$)	4.7×10^{11}	3.6×10^{11}			$(6.7 \pm 1.5) \times 10^{10}$
D + HF($v = 1$)	9.0×10^{11}	1.0×10^{11}			$(1.8 \pm 1.5) \times 10^{10}$
D + DF($v = 1$)	4.5×10^{11}	5.0×10^{10}			$(-1 \pm 8) \times 10^{10}$
D + HF($v = 0$)	7.5×10^{11}				$< 2.5 \times 10^8$

^a k_R denotes vibrational deactivation accompanied by F-atom abstraction by the incoming H or D atom.

^b k_N denotes vibrational deactivation without atom exchange.

For our experimental conditions, Reaction (2) will be driven far to the right at equilibrium, i.e., $K_{eq} = 3.3$, $[HF] = 6 \times 10^{-9}$ mol/cc and $[D] = 6 \times 10^{-9}$ mol/cc. However, no reduction in the laser-induced fluorescence from $HF(v = 1)$ in the presence of D atoms was observed. Such a reduction would be expected if $HF(v = 0)$ decreased in concentration. With a generous 10% uncertainty assigned to the change in the $[HF(v = 0)]$, $\Delta[HF(v = 0)]/[HF(v = 0)] \leq 0.1 \approx k_2[D]t$. With $t = 20$ msec and $[D] = 6 \times 10^{-9}$ mol/sec, it can be concluded that $k_2 \leq 1 \times 10^9$ cc/mol-sec. Another and more sensitive experiment consists of probing for $DF(1 \rightarrow 0)$ laser-induced fluorescence, i.e., DF appearance, under the conditions previously described for $HF(v = 0)$ disappearance. No fluorescence was detected. Our calibrated threshold detectivity for $DF(v = 0)$ is 3×10^{-11} mol/cc. Therefore, $\Delta[DF(v = 0)]/[HF(v = 0)] \leq 5 \times 10^{-3} \approx k_2[D]t$. This calculation implies that $k_2 \leq 2.5 \times 10^8$ cc/mol-sec. This latter limit is probably the more reliable.

IV. DISCUSSION

A. VIBRATIONAL-RELAXATION EXPERIMENTS

There is poor agreement between the experimental results for H-atom deactivation of HF($v = 1$) (Table 5). The value $1.4 \pm 0.4 \times 10^{11}$ cc/mol-sec for this study is smaller than the upper limit of $(7 \pm 4) \times 10^{11}$ cc/mol-sec reported by Kwok and Wilkins⁹ but larger than the upper limit of 9×10^9 cc/mol-sec reported by Quigley and Wolga.⁶ The experimental technique used by Quigley and Wolga is similar to that of this study, but they use ESR to detect the H atoms. The method of analysis is different in the two experiments, however.

When HF molecules are excited to their first vibrational level in the presence of H₂, there is an initial decay of the HF($v = 1$) as energy is transferred to H₂ vibrational excitation. At longer times, the populations of HF($v = 1$) and H₂($v = 1$) are vibrationally coupled, and both decay with an overall time constant determined by the combined ($V \rightarrow R, T$) processes.³ Quigley and Wolga observed no H-atom effect on either the first or the second decay time. From this observation, they concluded that $k_{\text{HF-H}}$ was less than one-half the $V \rightarrow R, T$ deactivation rate of HF($v = 1$) by H₂ ($k_{\text{HF-H}_2}^{V \rightarrow T} \leq 1.8 \times 10^9$ cc/mol-sec.^{2, 18} Our observations are similar because we saw essentially no change in the first decay, but different because we observed a decrease in the second decay time. Our preliminary modeling calculations show that this decrease is due predominantly

to deactivation of $\text{H}_2(v = 1)$ by H atoms¹⁴ and to the change in $\text{H}_2(v = 0)$ concentration with a subsequent shift in the $\text{H}_2(v = 1)$ and $\text{HF}(v = 1)$ concentrations.

Kwok and Wilkins⁹ studied the deactivation of $\text{HF}(v = 1)$ in the presence of H atoms in a discharge flow tube. Both $\text{HF}(v)$ and H were created by titrating F atoms with H_2 . An advantage of the laser-induced fluorescence technique is that H atoms can be produced independently of the $\text{HF}(v)$ and at much higher concentrations. The higher concentration of H atoms increases the contribution of $\text{H} + \text{HF}(v)$ relative to the other decay processes, i. e., spontaneous emission and $\text{V} \rightarrow \text{T}$ quenching by HF. Thus, the present experiment is a more sensitive probe of the relatively slow rate of destruction of $\text{HF}(v = 1)$ and $\text{DF}(v = 1)$ by H and D atoms.

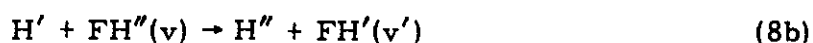
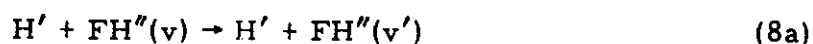
B. COMPARISON WITH TRAJECTORY CALCULATIONS

In addition to the results just cited for $\text{H} + \text{HF}$, a great deal of data exist regarding the $\text{F} + \text{H}_2$ system, including measurements of the absolute reaction rate for Reaction (1) and the distribution of vibrational energy in the product HF. Ab initio calculations of the potential-energy hypersurface have been made by Bender et al.²²⁻²⁴ Classical trajectory calculations for $\text{F} + \text{H}_2$ have been carried out by Jaffe and Anderson,²⁵ Muckerman,²⁶ and Wilkins²⁷ on various modifications of an LEPS surface. Wilkins also calculated rate coefficients for $\text{HF}(v)$ and $\text{DF}(v)$ deactivated by H and D.^{8, 21}

When the LEPS surfaces are calibrated against the experimentally determined activation energy for $\text{F} + \text{H}_2$, trajectory calculations give product vibrational distributions in good agreement with infrared chemiluminescence

and chemical-laser experiments.²⁶ The ab initio calculations of the $F + H_2$ potential surface gave a barrier height that is identical with the experimental activation energy of 1.7 kcal/mol. As Bender et al.²⁴ pointed out, this agreement is fortuitous, considering the precision of the calculations (~ 2 kcal/mol).

The agreement between trajectory calculations and our experimental results is not good in the case of $HF(v = 1)$ deactivation by H atoms. Wilkins⁸ in his calculation of H-atom deactivation of $HF(v)$ used the same LEPS parameters that he used in his description of the $F + H_2$ surface. However, the deactivation calculations are sensitive to a different portion of the potential energy hypersurface, i.e., H atoms colliding with the F end of HF.



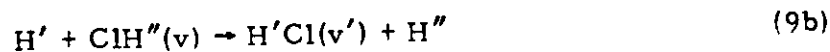
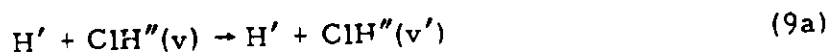
where $v > v'$. Reaction (8a) represents nonreactive deactivation of $HF(v)$, while (8b) represents reactive deactivation. Wilkins' calculations^{8,21} are summarized in Table 5 along with the experimental data for the four isotopic combinations of H(D) deactivation of $HF(v = 1)$ and $DF(v = 1)$. The present results represent the sum of Reactions (8a) and (8b) since $HF(v = 1)$ disappearance was monitored. Comparison of experiment with theory (Table 5) indicates that Reaction (8b), i.e., F-atom abstraction, is the major point of disagreement. As previously mentioned, Wilkins' LEPS surface has a low barrier height (~ 1.5 kcal/mol). In addition, the predicted rate coefficients

have large pre-exponential factors,²¹ indicating no important configurational constraints on the collision partners. The data reported here show that Wilkins' LEPS surface must differ significantly from the true surface in the region important to H-atom deactivation of HF(v) by F-atom exchange. Furthermore, this difference is probably in the barrier height, although experiments carried out at a single temperature do not prove this contention. Wilkins²⁸ has calculated a rate coefficient of 7.5×10^{11} cc/mol-sec for Reaction (2) as opposed to our measured value of less than 2.5×10^8 cc/mol-sec. The measured value indicates that the activation energy for F-atom exchange should be larger than 7 kcal/mol if an Arrhenius pre-exponential factor of 2.5×10^{13} cc/mol-sec is assumed. Calculations for an LEPS surface with such a large barrier would certainly result in a much smaller rate for reactive deactivation [Reaction (8b)] and would probably reduce the nonreactive rate [Reaction (8a)].

Several qualitative arguments can be made for a barrier height larger than the LEPS prediction for HFH. Potential energy surfaces determined for HXH intermediates are known to be critically dependent upon the exact method of calculation.²⁹ Many calculations have identified wells in the surfaces that have never been convincingly verified. Blais and Truhlar³⁰ recently carried out a valence bond calculation for DFH that explicitly treated the seven valence electrons, $2p_F^5 1s_{H_a} 1s_{H_b}$, and yielded a 14-kcal/mol potential barrier. This result contradicted Magee's earlier study³¹ in which he found a 30-kcal/mol potential well for HFH, when he used a $2p_F^1 1s_{H_a} 1s_{H_b}$ basis set. The 14-kcal/mol barrier reported by Blais and Truhlar³⁰ would

imply an activation energy of approximately 11 to 12 kcal/mol, considering the effect of zero point energy, leading to a room-temperature rate coefficient of less than 10^6 cc/mol-sec for F-atom exchange. This is consistent with the upper limit given in Table 5 for $D + HF(v = 0)$. Since the $v = 1$ level of HF lies 11.3 kcal/mol above $v = 0$, it is possible that there is insufficient energy in vibration alone to surmount the barrier for F-atom exchange. This hypothesis could account not only for the relatively slow rate at which H atoms deactivate $HF(v = 1)$ but also for the experimental observation of a much faster rate for $H + HF(v = 2 \text{ and } 3)$ ⁹ where sufficient energy certainly exists to open the reactive channel. At the present time, there have been no isotopic exchange experiments designed to evaluate the relative contribution of Reactions (8a) and (8b).

The experimental situation for $H + HCl(v'')$ is analogous to that for $H + HF(v'')$. Several determinations of the rate coefficients for $H + HCl(v = 0) \rightarrow H_2 + Cl$ [a closed channel for $H + HF(v = 0)$] have been made, and an upper limit for $H + HCl(v = 1) \rightarrow H_2 + Cl$ has been measured by Arnoldi and Wolfrum¹¹ [this process contributed less than 10% of the sum of Reactions (9a) and (9b)]. The experimental separation of reactive and nonreactive vibrational deactivation



has not been made. Experimental evidence for a low barrier height (~ 1 kcal/mol) for the HClD intermediate has been obtained by Wood³² for the reaction $\text{H} + \text{DCI}(v = 0) \rightarrow \text{D} + \text{HCl}(v = 0)$. Interestingly, the pre-exponential factor obtained was also small (3×10^{-5} times gas kinetic), resulting in a small room-temperature rate coefficient. Once again, many semi-empirical calculations show HClH to have a large attractive well.²⁹ Since the sum of the rate coefficients for Reactions (9a) and (9b) is very large ($\sim 4 \times 10^{12}$ cc/mol-sec), an attractive surface is more plausible than in the case of $\text{H} + \text{HF}$. It would indeed be interesting to determine whether ab initio calculations yield a marked difference in the barrier height (or well depth) for HClH and HFH. Such calculations are in progress for HFH.³³

Experimental rate coefficients have been measured for the removal of $\text{HF}(v = 1)$ and $\text{DF}(v = 1)$ by H and D atoms. These rate coefficients are much smaller than were predicted by classical trajectory calculations. Our evidence strongly suggests that the barrier height for F-atom exchange is larger than the 1.5 kcal/mol used in the calculations. The present results indicate the need for additional theoretical investigation of the potential energy surface for HFH.

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